



**29th American Society for Gravitational and Space Research
and 5th International Symposium for Physical Sciences in Space**

Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport in Low Gravity

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ISS: MSRR Science



Scientific Objectives

1. To establish the relative contributions of gravity-driven fluid flows, both in liquid and vapor, to (1) the non-uniform incorporation of impurities and defects and (2) the deviation from stoichiometry and (3) the compositional variation observed in the grown crystals.
2. To assess the self-induced strain developed during processing at elevated temperatures and retained on cooling caused by the weight of the crystals.
3. The relation between fluid phase processes and the generation of defects in a grown crystal is an outstanding problem in materials growth. Studies in microgravity will be compared with modeling and will lead to a greater understanding of the processes involved.

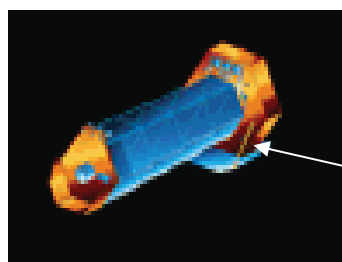


Crystal Growth Activities at MSFC

Technological significance:

Growth (melt and vapor) and characterization of II-VI compounds semiconducting materials, such as HgCdTe, HgZnTe (for IR detectors), CdS and ZnO (for UV detector), ZnSe, ZnSeTe (for green/blue laser), CdTe and CdZnTe (for x-ray, gamma ray detectors).

II	VI
Zn	O
Cd	S
Hg	Se
	Te



**CdZnTe
FPA**



**X and gamma
ray telescope**


Contributors:

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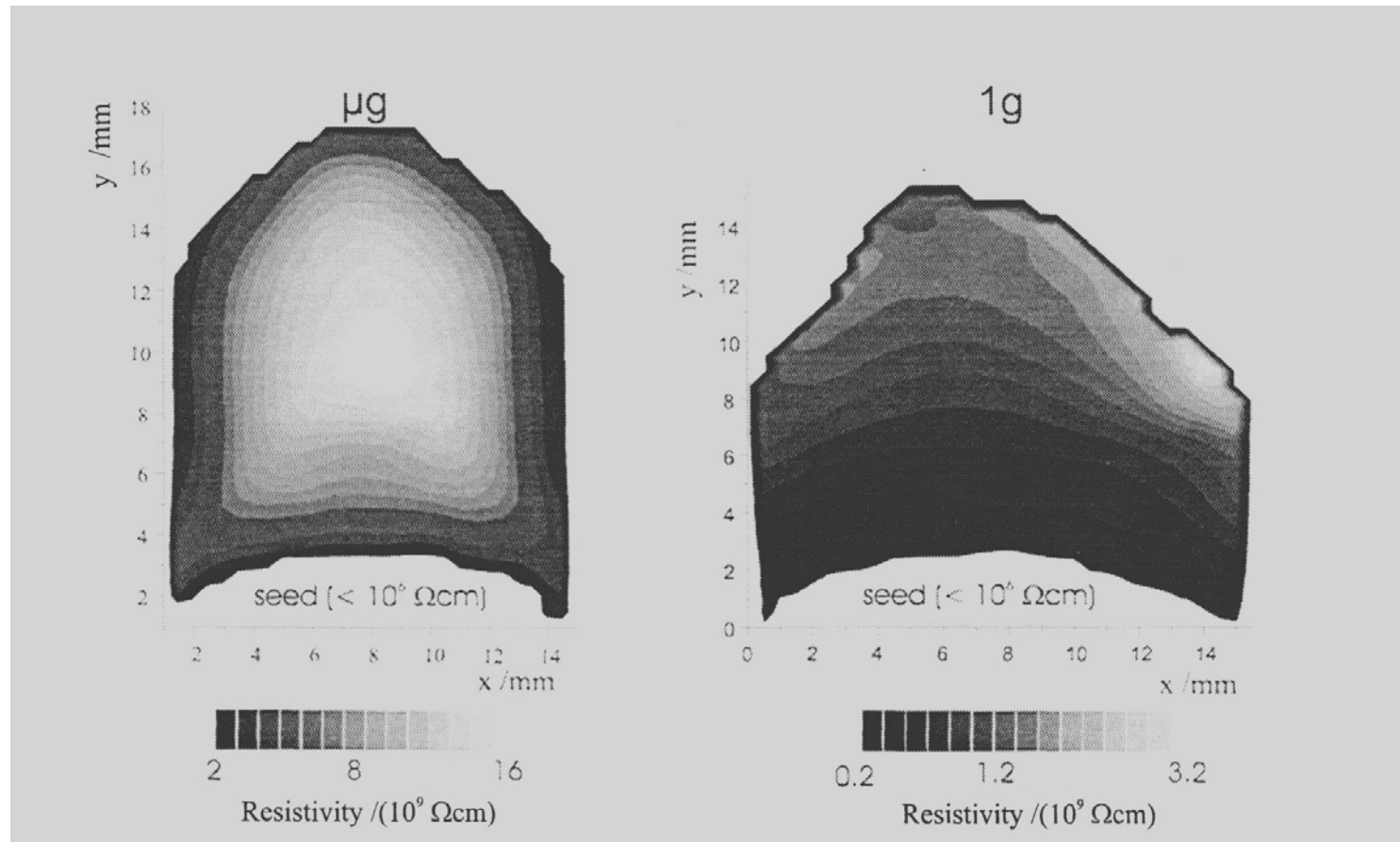


II-VI semiconducting compounds grown at MSFC

Compounds	HgTe	HgCdTe	CdTe	CdZnTe	ZnTe	CdS	ZnSe	ZnS
Melting points (°C)	670	700	1092	1130	1292	1397	1526	1718
Melt growth								
PVT growth temperature (°C)			850		1000	985	1120	1150



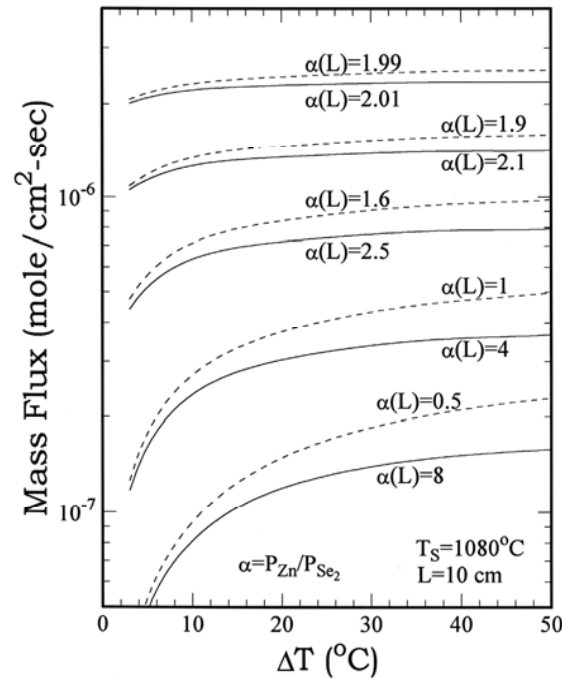
Crystal growth by Physical vapor Transport



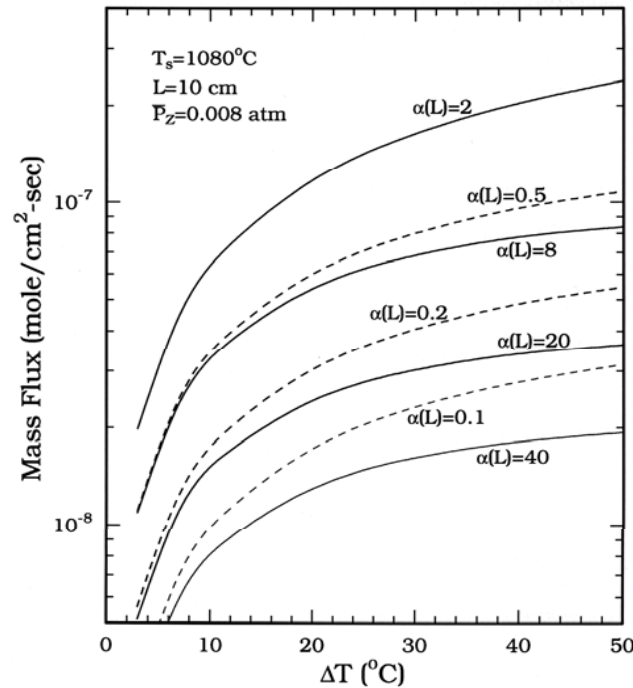
Results of Cl doped CdTe crystal grown by PVT in microgravity on the EUREKA-1 mission. The plots are two dimensional resistivity distributions mapped across the axial direction of two crystal wafers. The wafer on the left was grown in the microgravity environment, while the wafer on the right was grown on Earth. (Benz, et al. 1997)



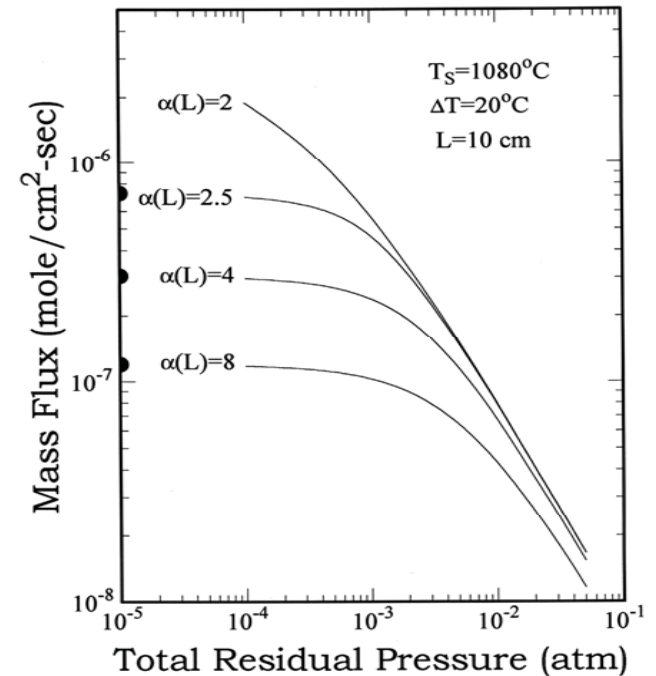
One-Dimensional Diffusion model of PVT



Calculated mass flux of ZnSe as a function of ΔT and different values of $\alpha(L)$. The source temperature was 1080 °C. Solid lines are for $\alpha(L) > 2$ and dashed lines are for $\alpha(L) < 2$.



Calculated mass flux of ZnSe as a function of ΔT under the same conditions except a residual gas pressure of 0.008 atm is present in the system.



Calculated mass flux of ZnSe as a function of residual gas pressure for source temperature at 1080 °C and different values of $\alpha(L)$.

Su, et al. (1998); Sha et al. (1995)



Summary of one dimensional diffusion analysis

- Four experimentally adjustable parameters, the source temperature, the deposition temperature, the partial pressure ratio over source and the residual gas pressure, determine the diffusive mass flux of a PVT system.
- However, two of these four parameters, the partial pressure ratio over source and the residual gas pressure, are more critical than the others. As will be shown, these two parameters are critically dependent on the proper heat treatments of the starting materials for optimum mass flux.



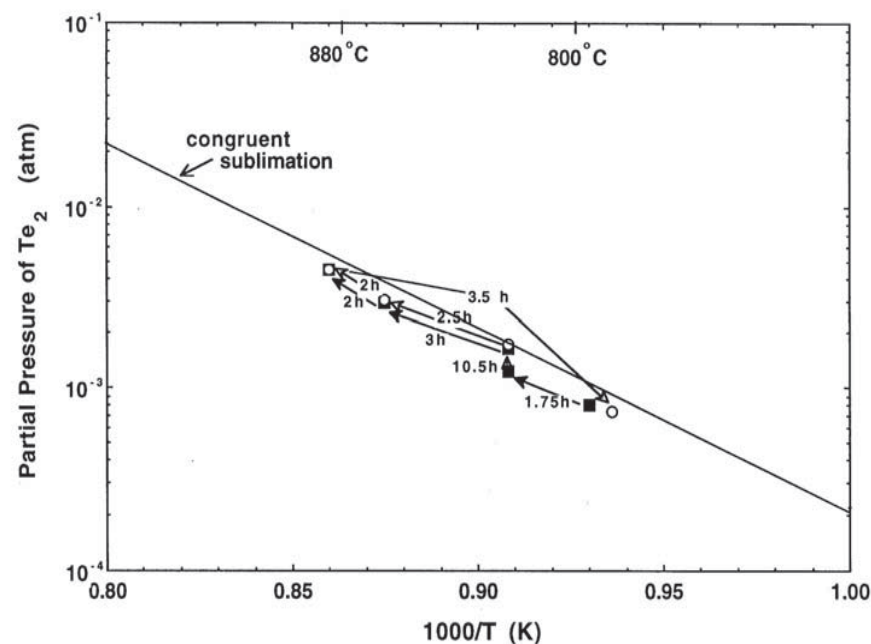
Heat Treatment of CdTe Starting Materials

Table 2. Amounts of CdTe loaded, heat treatment conditions, the measured partial pressure of Te_2 , P_{Te_2} , and the calculated pressure ratio, $P_{\text{Cd}}/P_{\text{Te}_2}$, at 870 °C for as-synthesized

and heat treated batches.

cell	amount of CdTe (g)	heat-treated temperature (°C)	heat-treated duration (min)	P_{Te_2} (atm) at 870 °C	$P_{\text{Cd}}/P_{\text{Te}_2}$ at 870 °C
6	15.0	-	-	4.06×10^{-3}	1.92
7	15.0	-	-	1.65×10^{-1}	0.00742
7A	13.0	870	8	3.44×10^{-3}	2.47
9	12.4	-	-	8.90×10^{-2}	0.0187
10	14.9	-	-	4.95×10^{-3}	1.43
10A	20.3	870	8	2.74×10^{-3}	3.47
11	6.9	-	-	1.51×10^{-2}	0.268
11A	20.0	860	8	2.96×10^{-3}	3.11
13A	17.9	800	8	4.18×10^{-3}	1.84

measured partial pressure of Te_2 for cell 10A



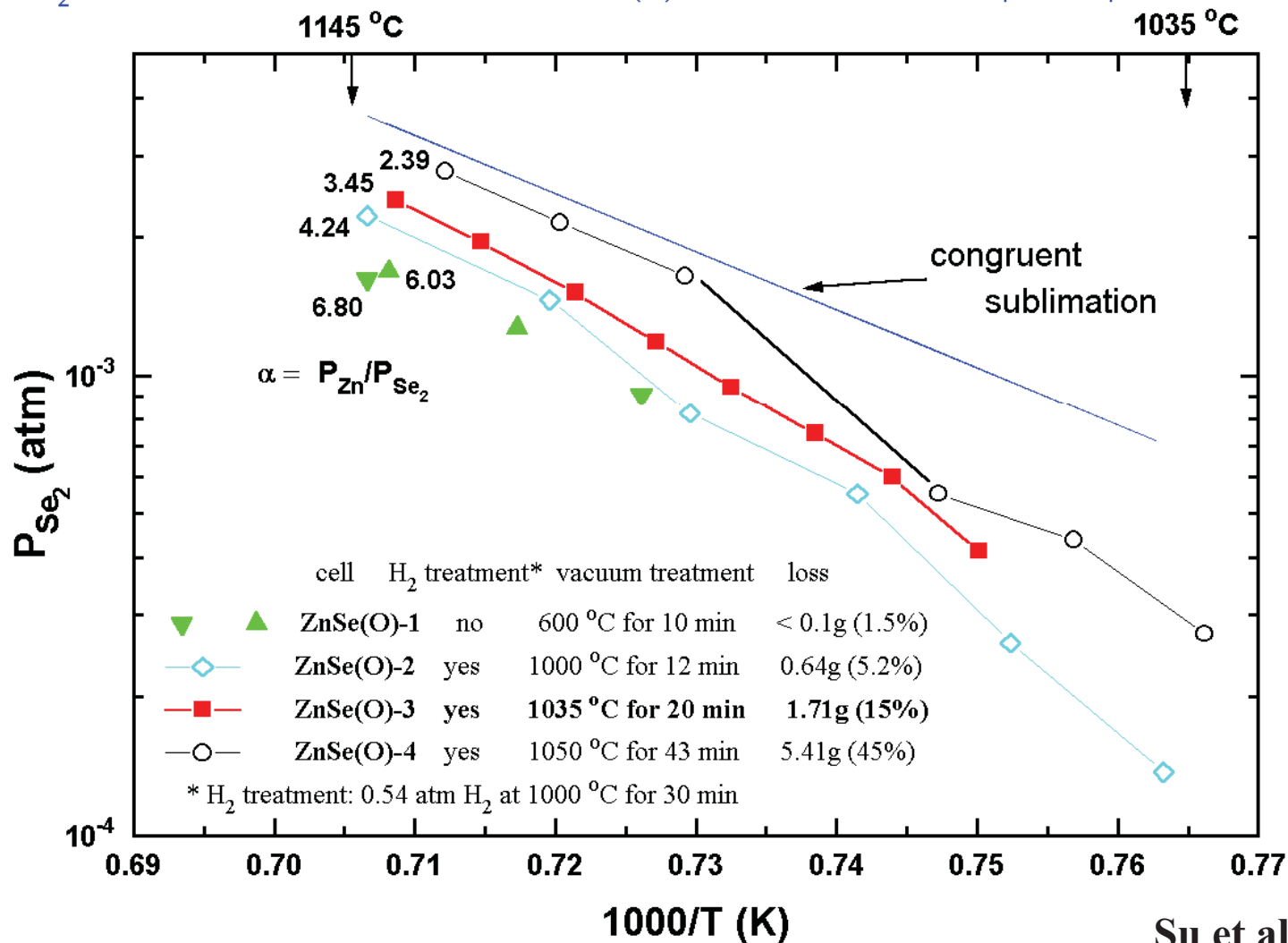
Su et al. (1998)



Optimum Heat Treatments of Starting Materials

P_{Se_2} in equilibrium with ZnSe for various optical cells

H_2 reduction and vacuum treatments for ZnSe(O)-3 established to be the optimum procedure

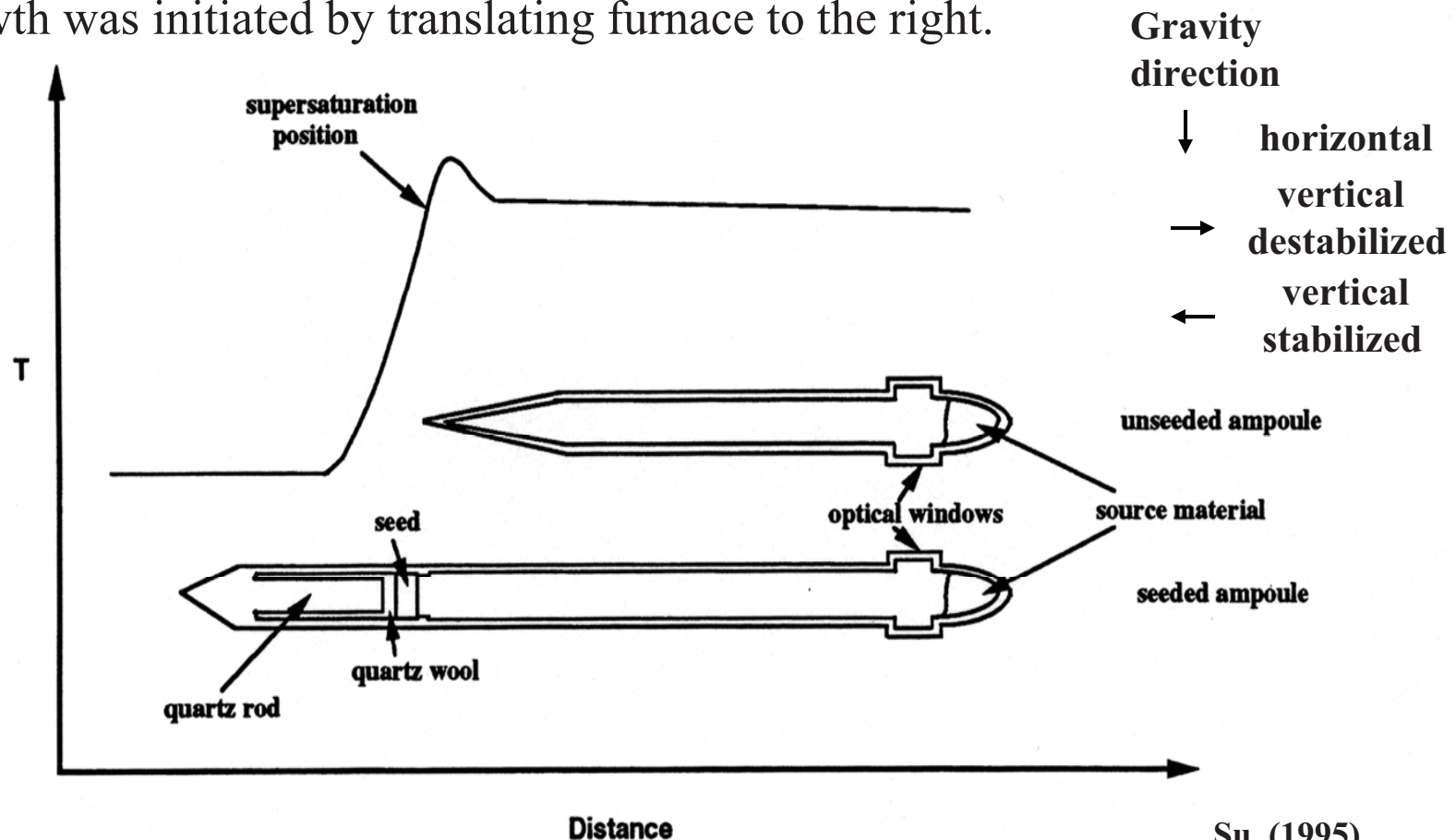


Su et al. (1998)



Physical Vapor Transport: temperature profile and initial ampoule positions

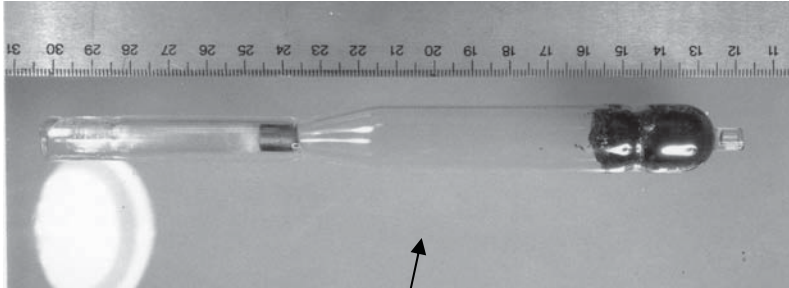
- The growth ampoules can be equipped with optical windows to confirm the stoichiometry of the starting material before growth.
- The thermal profile, with a maximum in the middle, was provided by a three-zone furnace with an adiabatic zone between central and cold zones.
- Growth was initiated by translating furnace to the right.



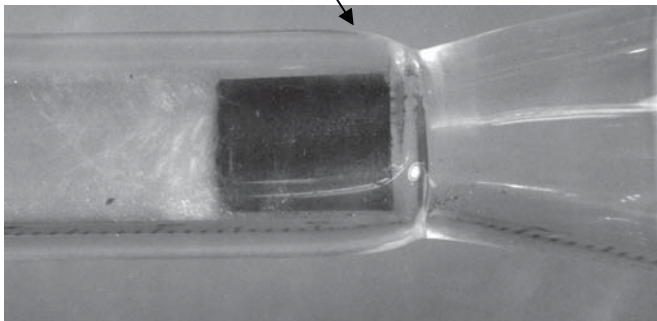
Su (1995)



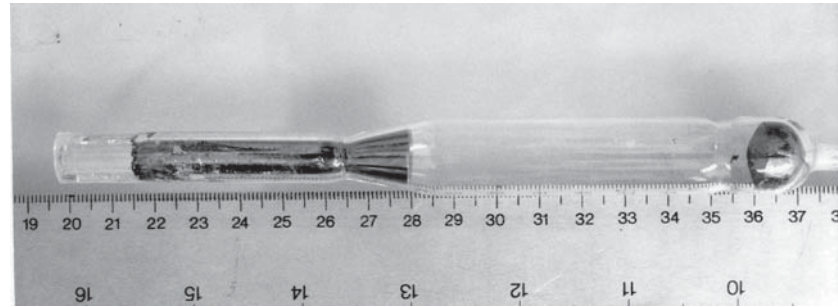
Steps of PVT Seeded Growth of CdTeS-14



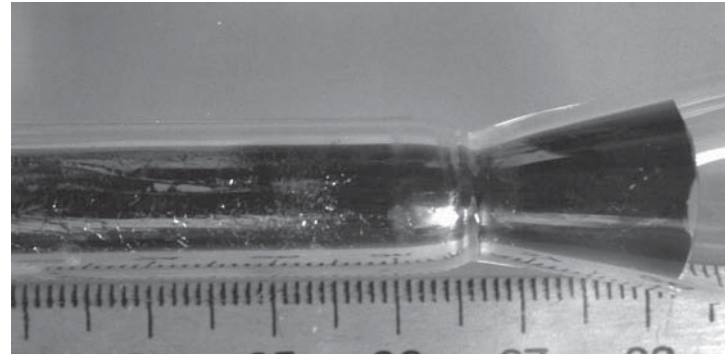
1. ampoule as loaded



2. ampoule after soaking at saturated position for 12 hours



3. reinsert ampoule and process PVT growth

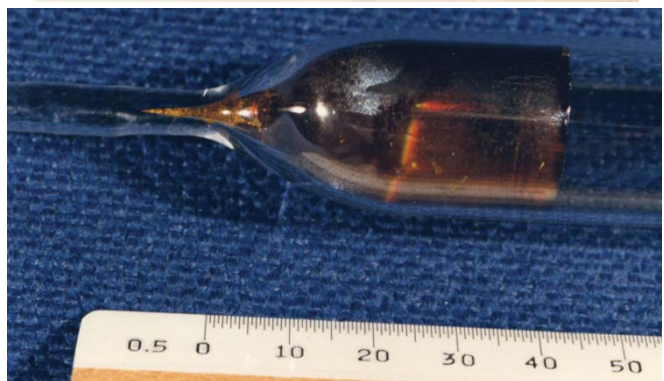


The initial position of the growth ampoule needs to be carefully located so that (1) to avoid spontaneous nucleation (2) to sublime part of the single crystal seed but (3) not completely dissolve the seed.

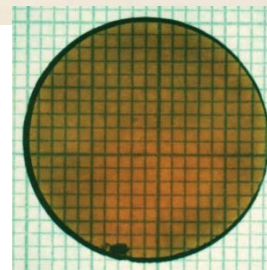
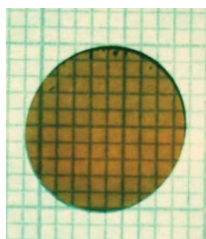


PVT Growth of Various Semiconductors

unseeded growth of CdS



seeded growth of CdS



unseeded growth of PbSe



unseeded growth of ZnTe

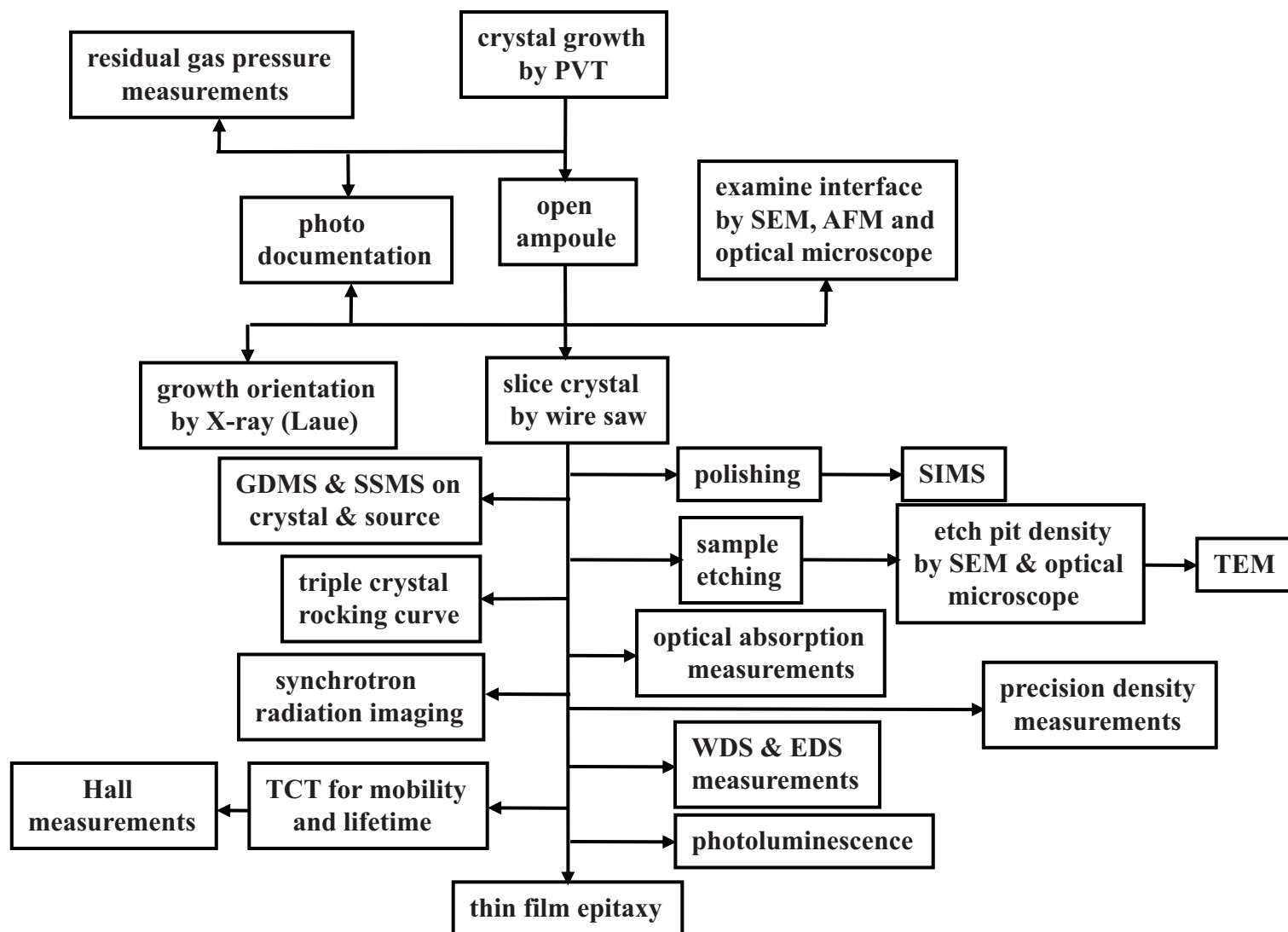


PVT Growth of ZnSe and Related Ternary Compounds

1. Self-seeded growth of ZnSe in vertical (stabilized and destabilized) and horizontal configurations
2. Seeded growth of ZnSe in vertical and horizontal configurations
3. Self-seeded growth of Cr-doped ZnSe in vertical and horizontal configurations
4. Self-seeded growth of ZnSeTe in vertical and horizontal configurations
5. *In-situ* and real-time optical monitoring of seeded growth in a horizontal configuration



Flow chart of sample characterization plan





Gravity Effects on the Grown Crystals

Effects were studied by comparing the following characteristics of horizontally and vertically grown ZnSe crystals in :

- Grown crystal morphology : contactless growth for the horizontal configuration.
- Surface morphology of the grown crystals was examined by SEM and AFM. (growth was terminated by stopping furnace translation, lowering the source temperature by 10 °C and then cooling the thermal profile at the same rate)
- Segregation and distribution of defects and impurities in the grown crystals was determined by photoluminescence, SIMS and precision density measurements.



Gravity Effects on the Grown Crystals

Morphology of the as-grown crystals:

- I. Self-seeded ZnSe: Crystals grown in the horizontal configuration grew away from the ampoule wall with large (110) facets tend to align parallel to the gravitational direction. Crystals grown in the vertical configuration grew in contact with the wall to the full diameter.
- II. Seeded ZnSe: the as-grown seeded crystals for the horizontal and vertical configurations showed similar characteristics in the morphology as described above for the self-seeded growth.

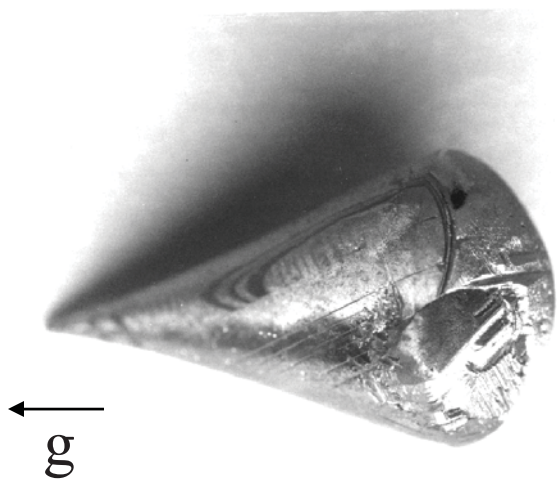
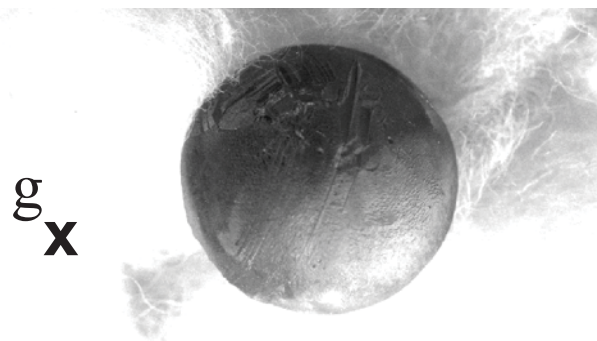
As-grown surface morphology:

- I. As-grown surface of horizontally grown crystals was dominated by (110) terraces and steps (identified to be (221) in one case).
- II. As-grown surface of the vertically grown
 - (a) Crystals showed granular structure with nanotubes (200nm OD, 75nm ID, 25nm in height for one case on ZnSe) on the top.
 - (b) Some crystals showed a network of high plateau with each island 30 – 70mm in diameter and 3.5mm in height. Numerous nuclei were observed with diameter 20 - 50nm and height of 1 - 7nm on top of these islands.



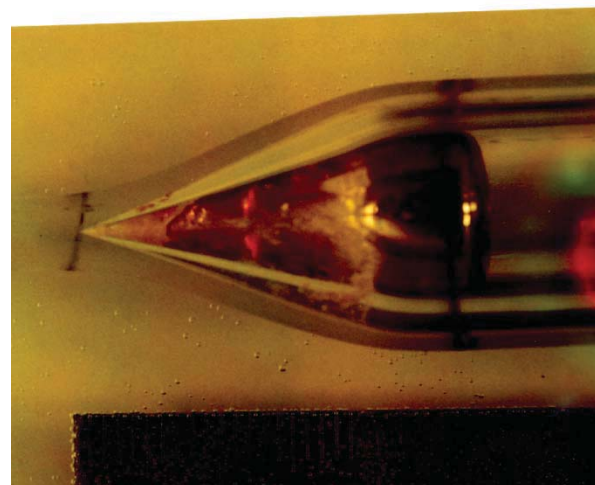
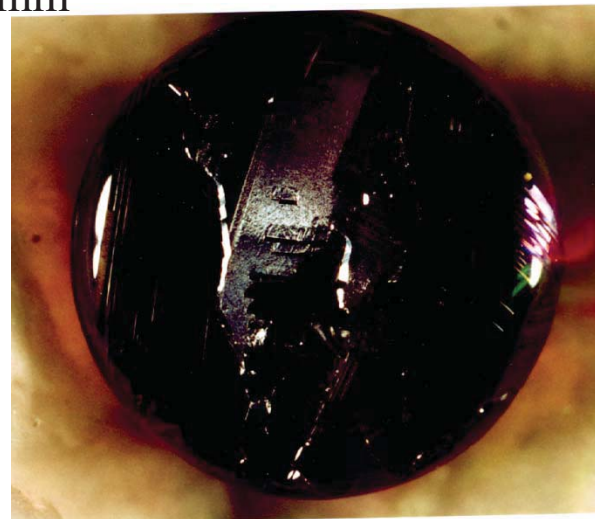
Morphologies of Self-seeded Vertically Grown ZnSe Crystals

ZnSe-25: vertically stabilized



ZnSe-31: vertically destabilized

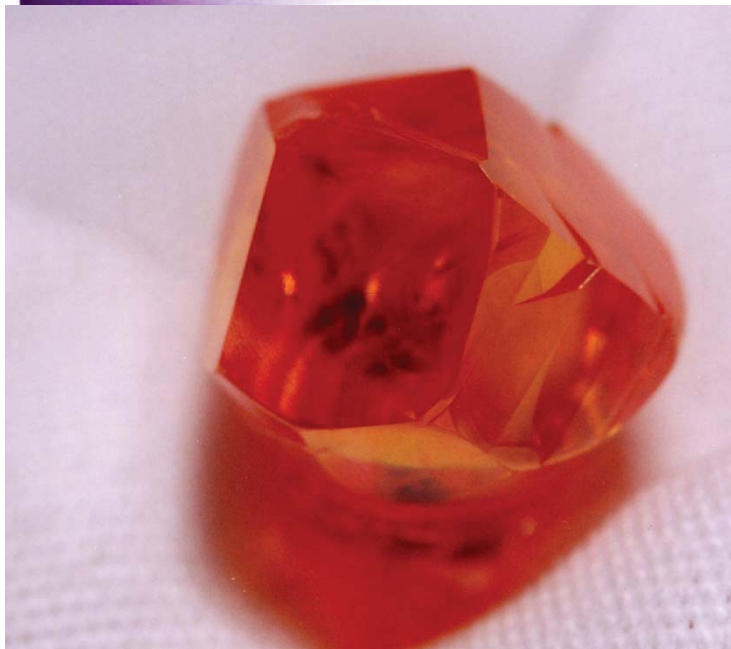
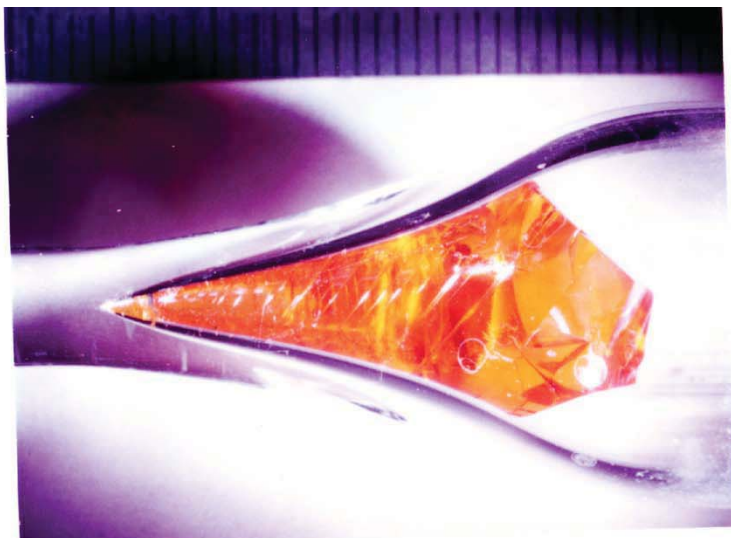
ampoule ID: 15mm



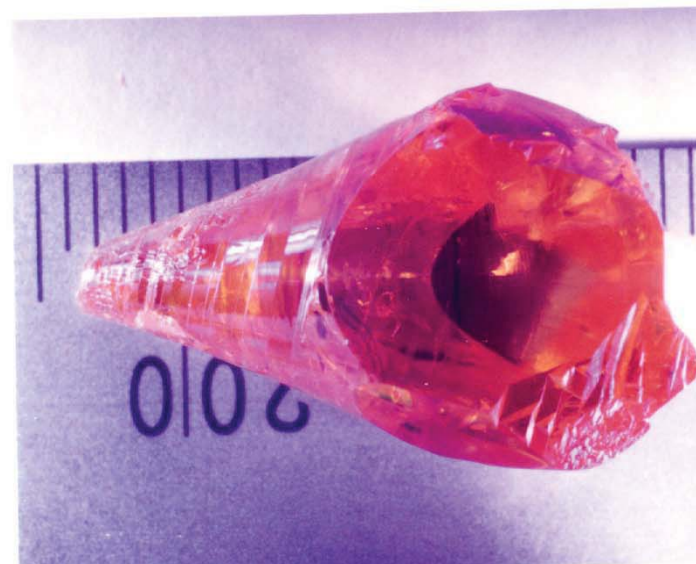
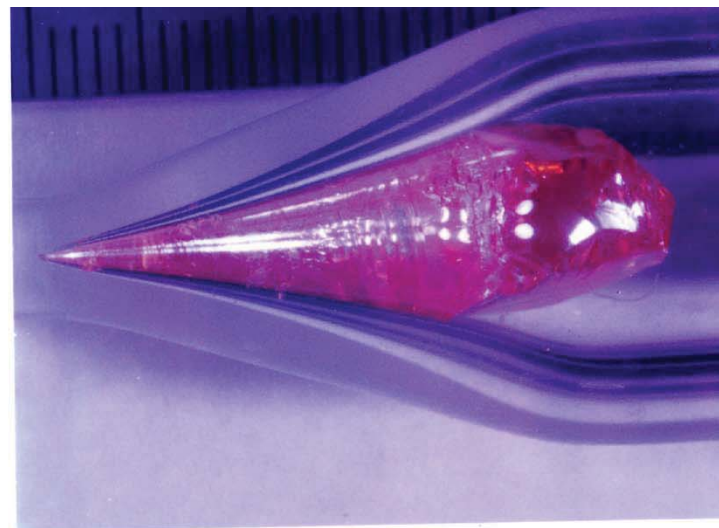


Morphologies of Self-seeded Horizontally Grown ZnSe Crystals

ZnSe-44



ZnSe-43

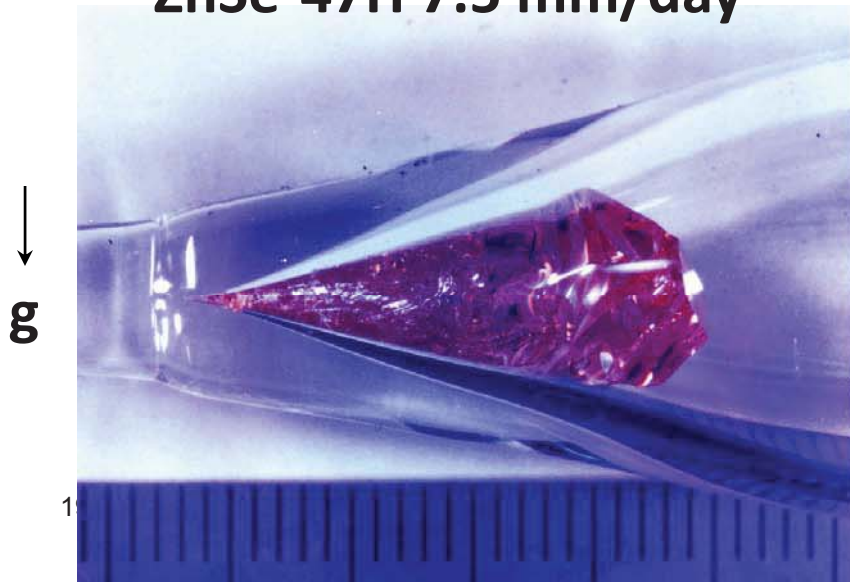




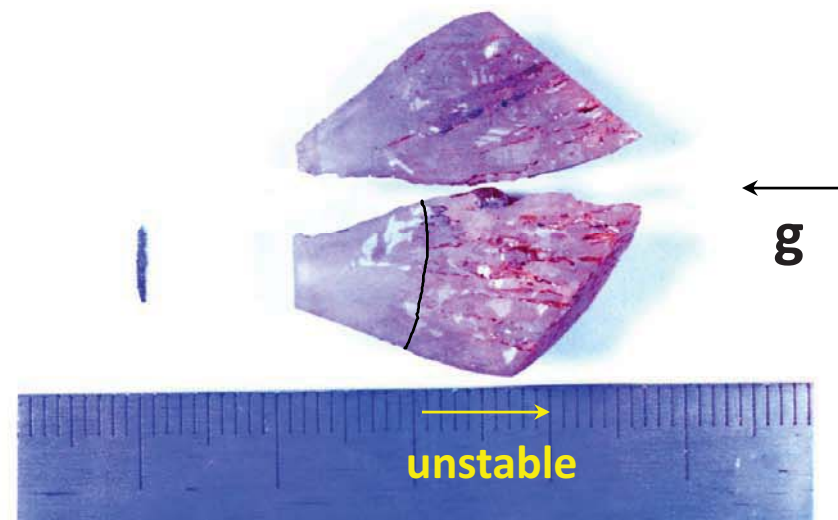
Gravity Effects on As-grown crystal morphology

- For furnace translation rates higher than the mass flux:
 - In the horizontal configuration the crystal maintained the growth surface morphological stability by (1) self-adjusting the degree of supersaturation to increase the mass flux or/and (2) by reducing the cross section area of the grown crystal.
 - In the vertical configuration the crystal growth surface became morphologically unstable with voids and pipes embedded.

ZnSe-47H 7.5 mm/day

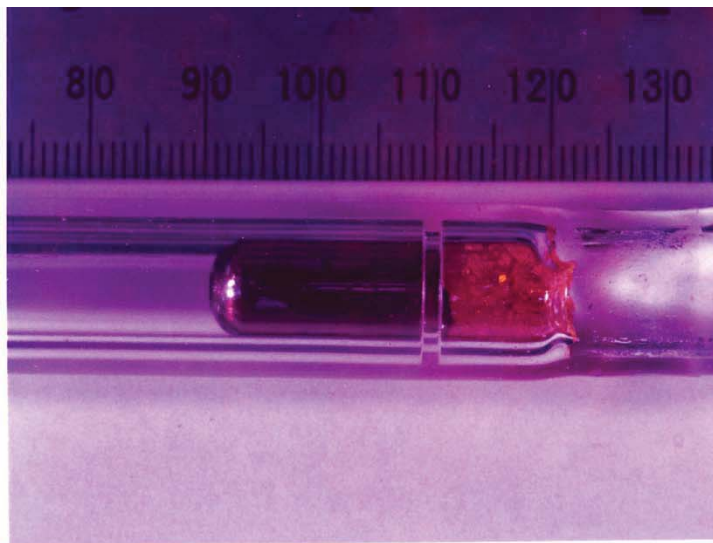


ZnSe-35V 11.4 mm/day

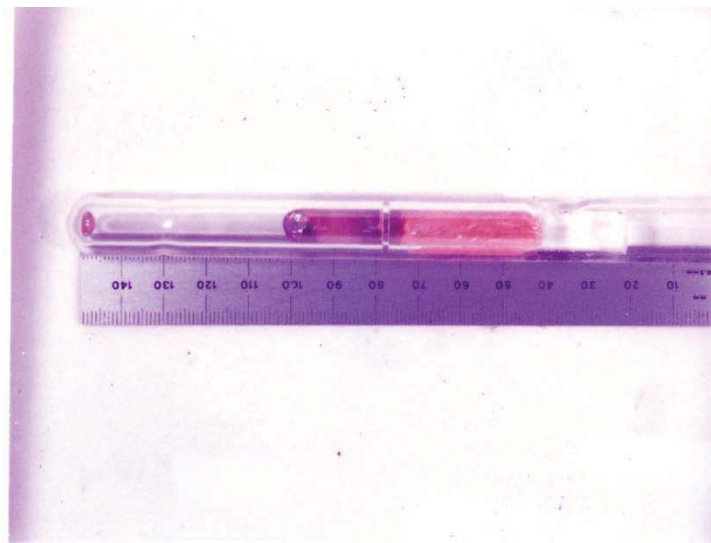




Morphologies of seeded vertically grown ZnSe crystals



ZnSe(S)-9V



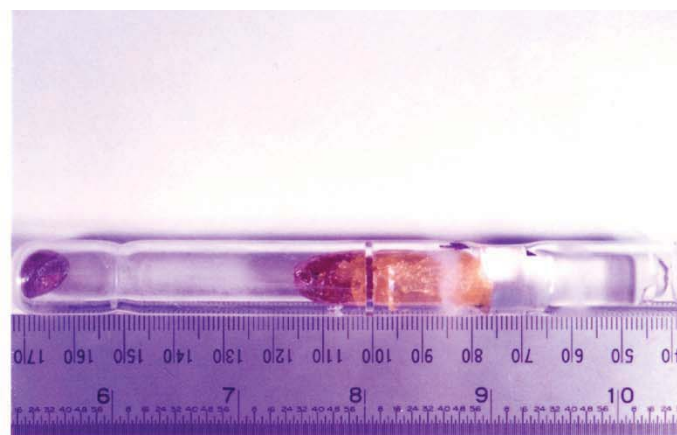
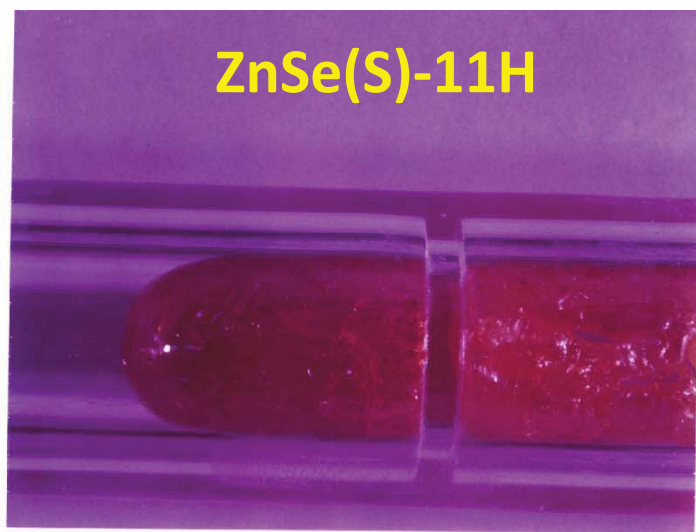
ZnSe(S)-12V





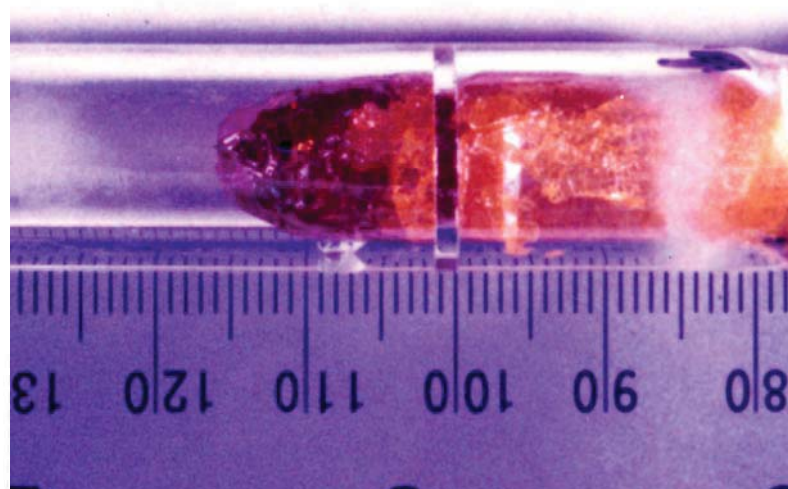
Morphologies of the seeded horizontally grown ZnSe crystals

g
x



g
↓

ZnSe(S)-13H





Gravity Effects on Impurities and Defects Distribution

I. Results from SIMS mappings :

For the horizontally grown self-seeded ZnSe crystal [Si] and [Fe] showed clear segregation toward the bottom on the wafer cut axially along the growth axis.

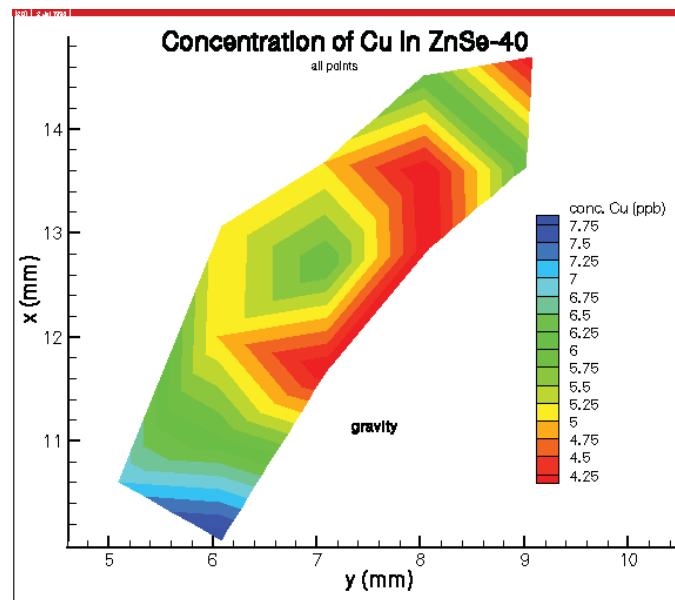
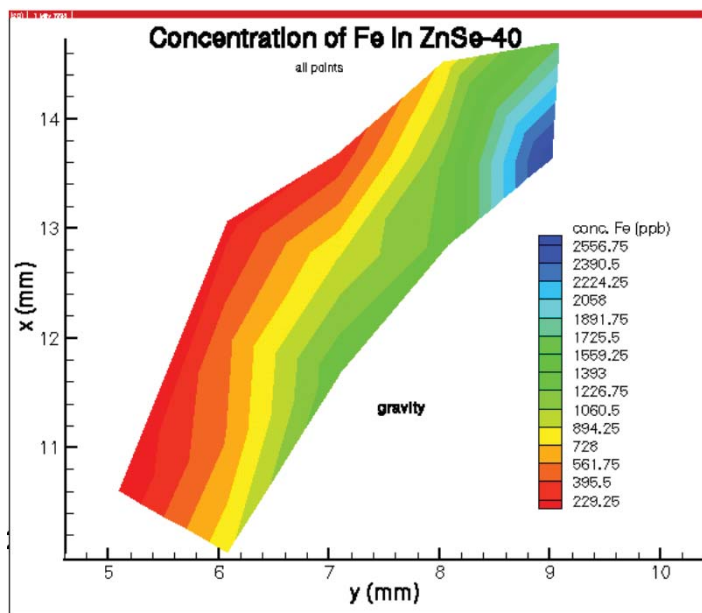
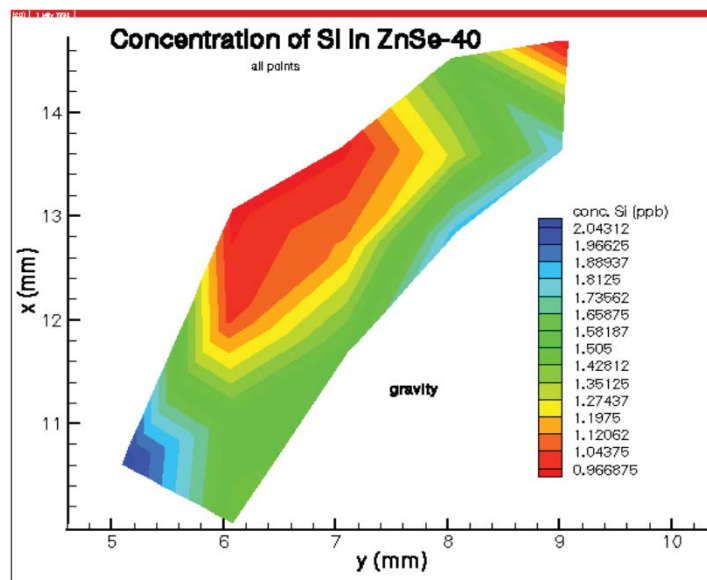
For the vertically grown seeded ZnSe crystal [Si] and [Cu] showed segregation toward the edge of the wafer cut perpendicular to the growth axis .

II. Mappings of PL near band edge intensity ratios indicated:

- (1) All the horizontally-grown crystals showed the following trends in the radial and axial segregation of [Al] and $[V_{Zn}]$:
[Al] segregates radially toward the top and axially toward the first grown region and $[V_{Zn}]$ segregates radially toward the bottom and axially toward the last grown region.
- (2) The as-grown surface of the seeded vertically stabilized grown crystal showed [Al], [Li or/and Na] and $[V_{Zn}]$ segregate radially toward the center.
- (3) The as-grown surface of the self-seeded vertically destabilized grown crystal showed [Al] and $[V_{Zn}]$ segregate radially without an apparent pattern.

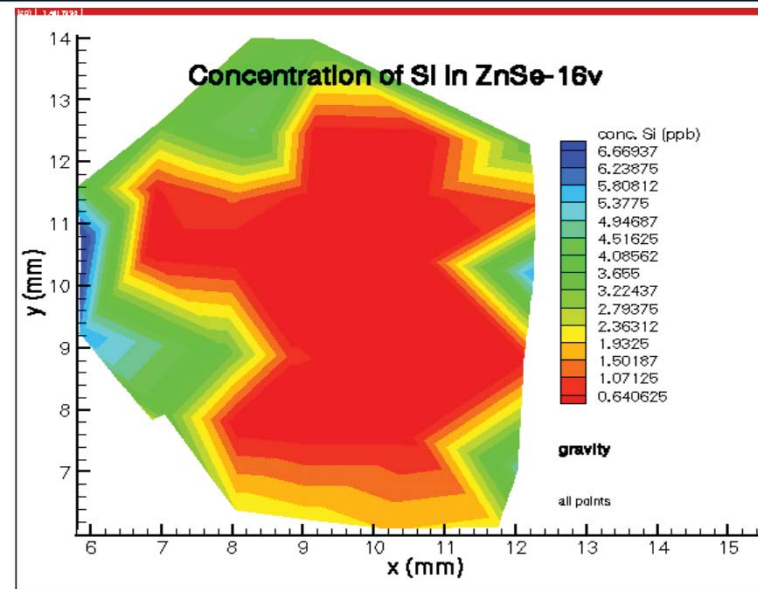


Impurities Distribution by SIMS (horizontally grown)

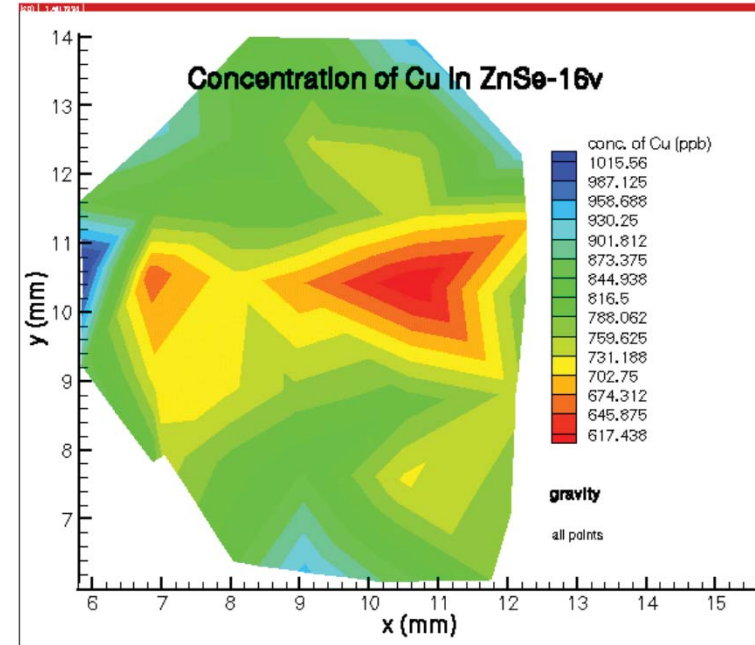
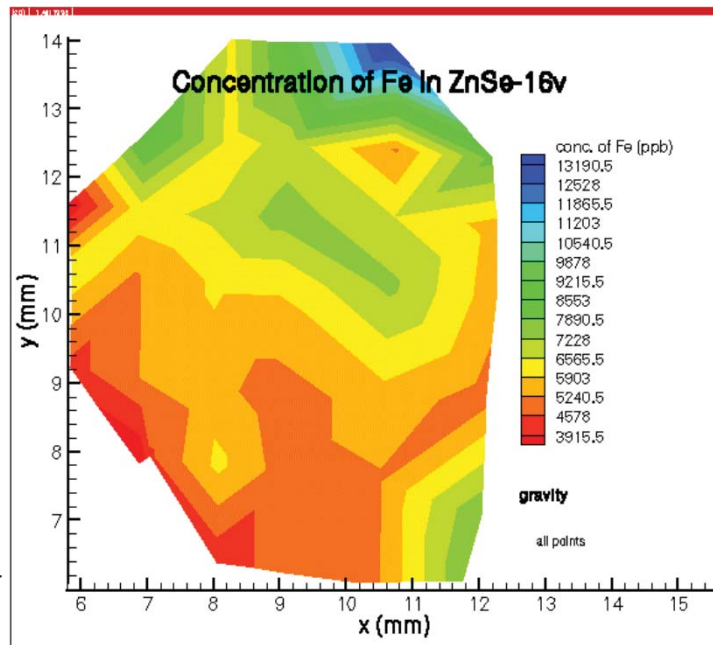




Impurities Distribution by SIMS (vertically grown)



X
gravity and
growth direction





Summary on the I_2 and I_1^{deep} emissions

I_2 emission:

- I_2 , the exciton bound to substitutional donor, emission in our ZnSe samples can be attributed mainly to Al impurity, with $A(I_2)/A(F_x) = 4.88$ corresponding to 1700 ppb, atomic, or $7.46 \times 10^{16} \text{ cm}^{-3}$.
- Isshiki et al. (1991) gave the expression between intensity ratio $(I_2)/(I_{F_x})$ and N_D :

$$\log_{10}(I_2/I_{F_x}) = -22.0775 + 1.46268 \log_{10} N_D (\text{cm}^{-3})$$
- Therefore, $(I_2/I_{F_x}) = 82 [A(I_2)/A(F_x)]$

I_1^{deep} emission:

- I_1^{deep} is related to exciton bound to V_{Zn} deep acceptor and $[V_{\text{Zn}}]$ is proportional to $A(I_1^{\text{deep}})/A(F_x)$.
- The reaction during Zn vapor annealing:

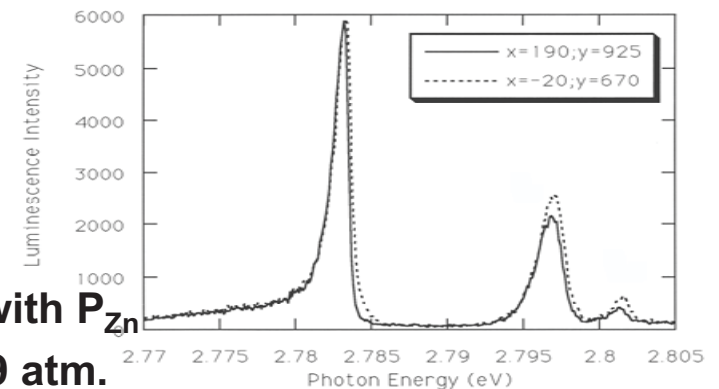


$$K = [V_{\text{Zn}}] \times P_{\text{Zn}} = K_1 A(I_1^{\text{deep}})/A(F_x) \times P_{\text{Zn}}$$

- The ZnSe samples were annealed at 1104 °C:

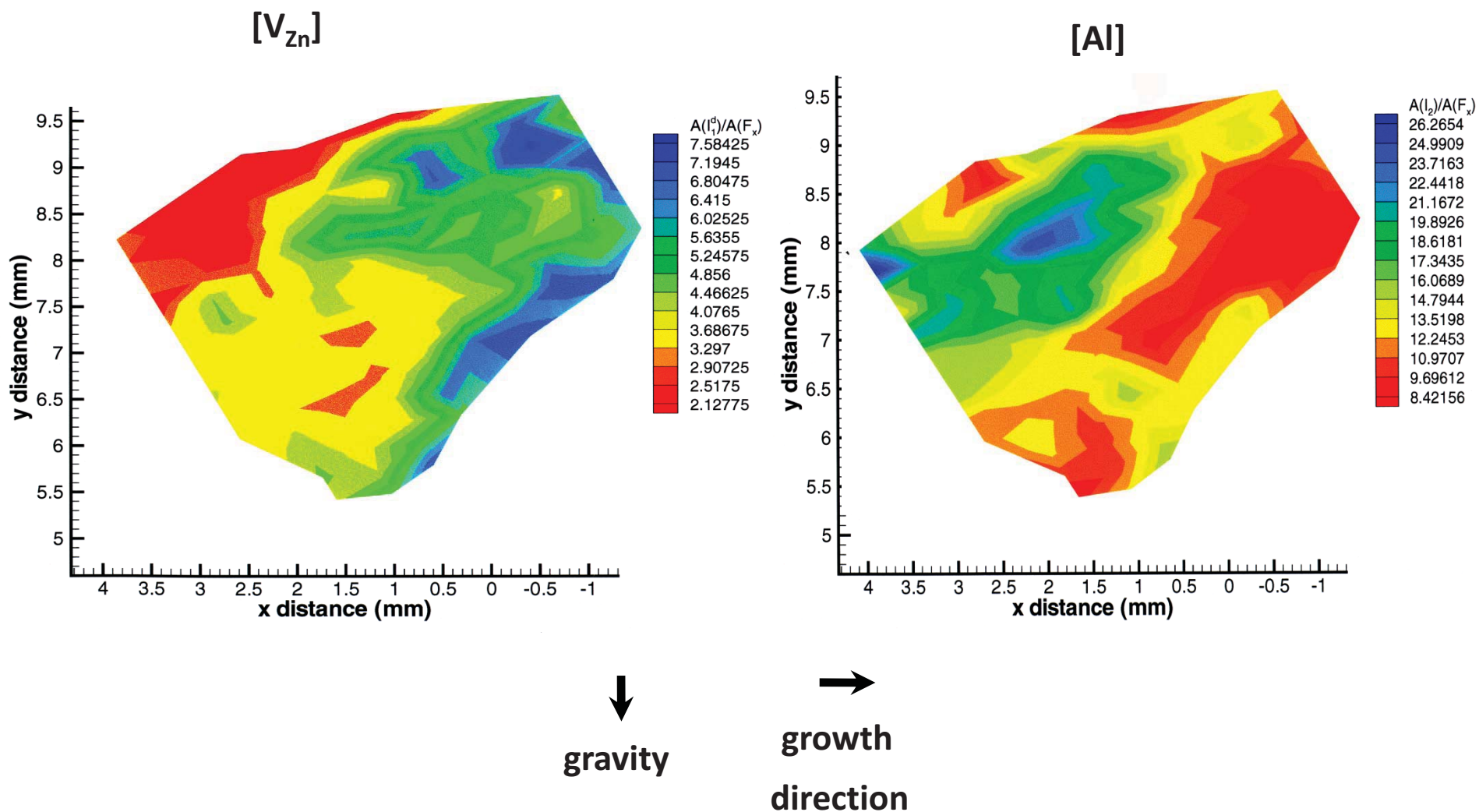
- $A(I_1^{\text{deep}})/A(F_x) = 7.52$ when sample is in equilibrium with $P_{\text{Zn}} = 6.1 \times 10^{-3} \text{ atm}$ ($\alpha = 6.05$) $A(I_1^{\text{deep}})/A(F_x) \times P_{\text{Zn}} = 0.0459 \text{ atm}$.

- $A(I_1^{\text{deep}})/A(F_x) = 5.18$ when sample is in equilibrium with $P_{\text{Zn}} = 9.0 \times 10^{-3} \text{ atm}$ ($\alpha = 19.43$) $A(I_1^{\text{deep}})/A(F_x) \times P_{\text{Zn}} = 0.0466 \text{ atm}$



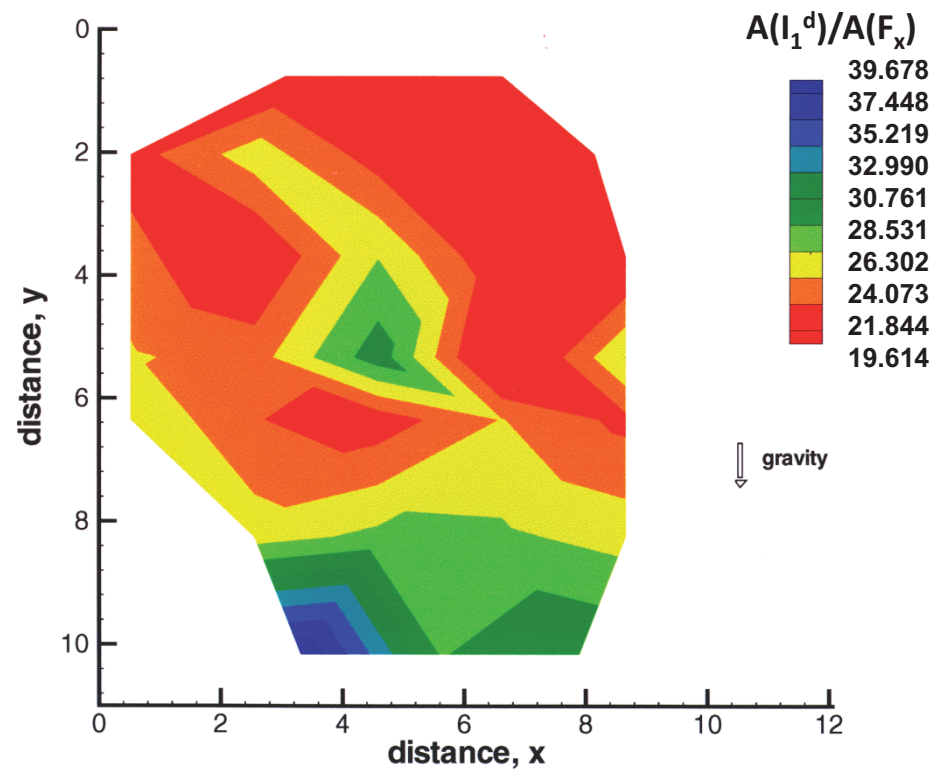
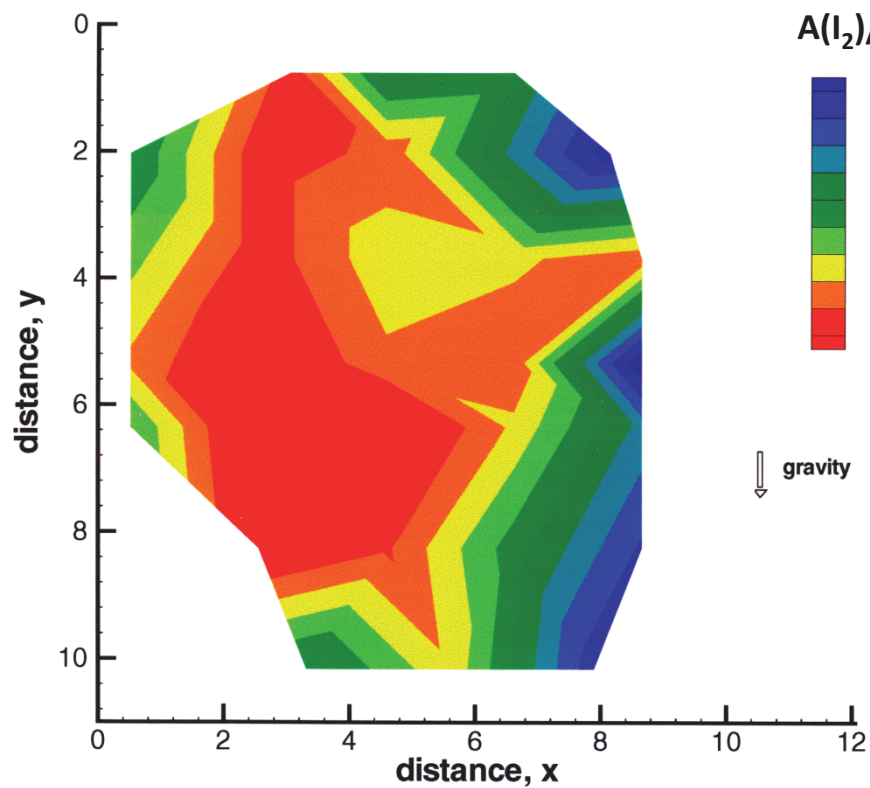


Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)





Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)

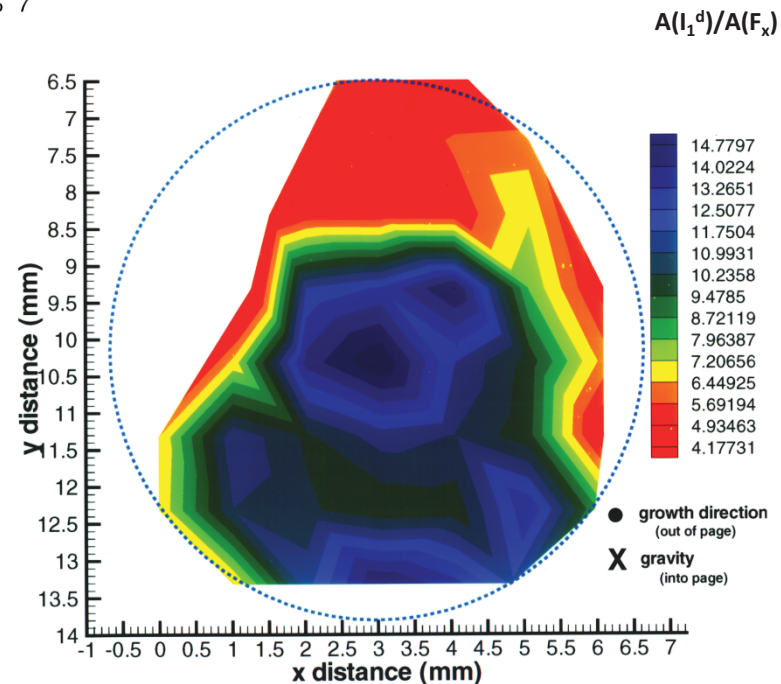
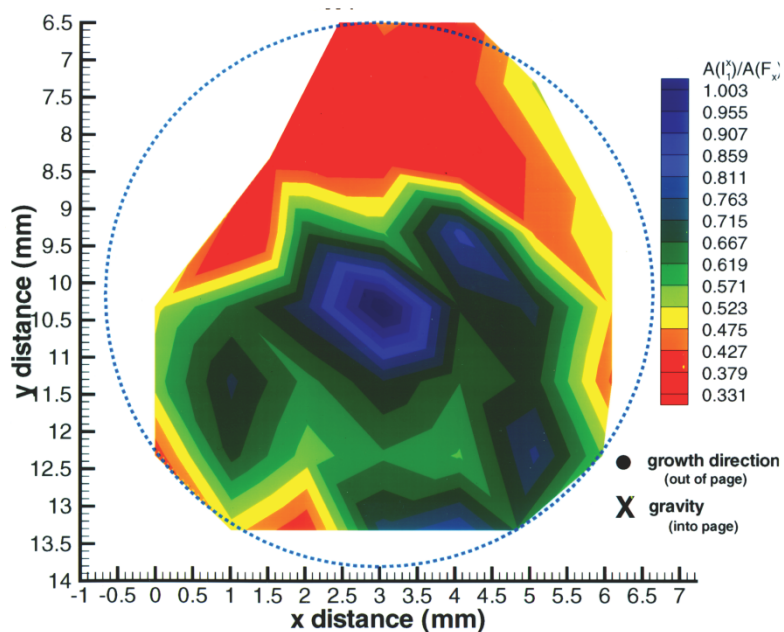
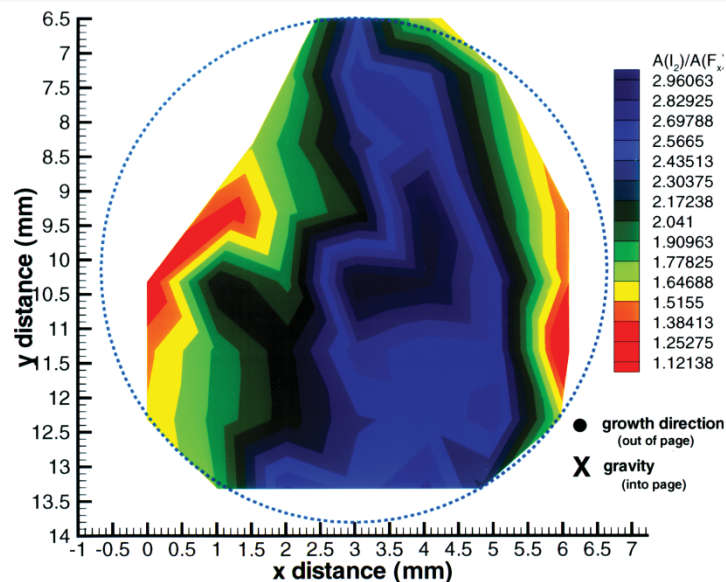


↓
gravity

X
growth
direction



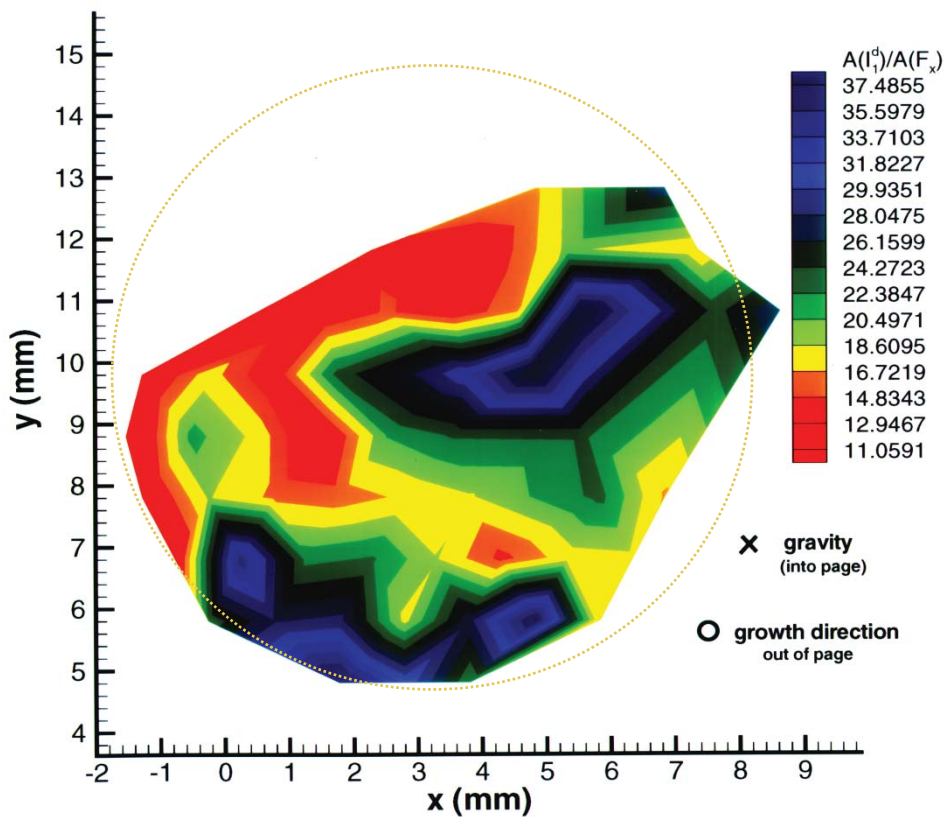
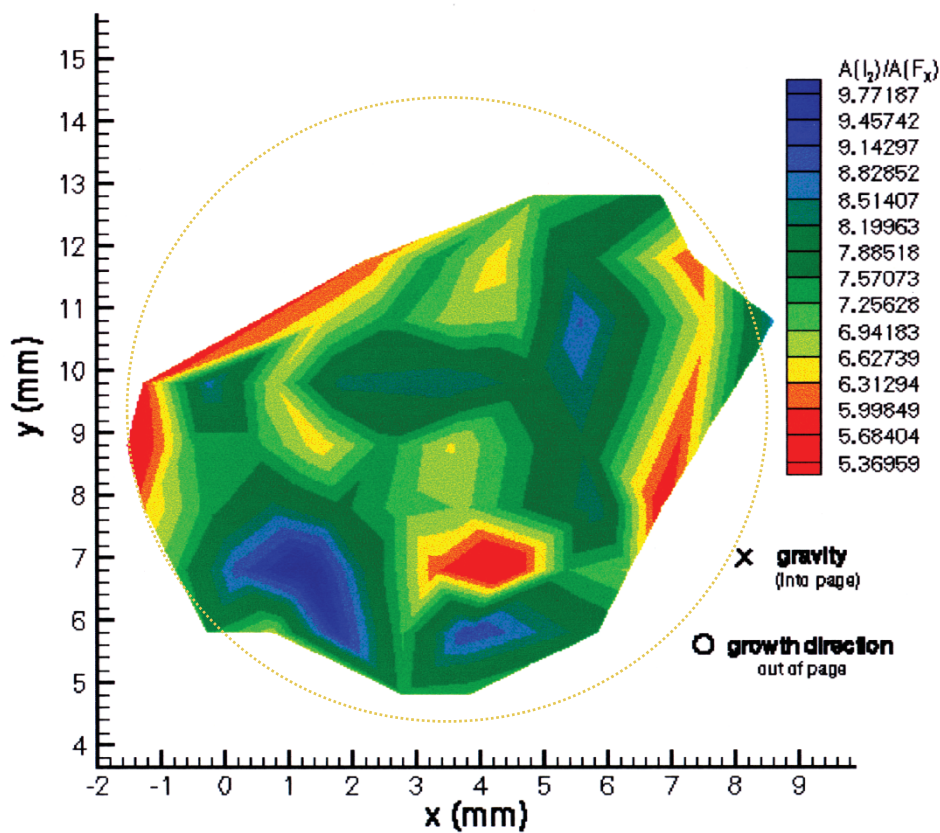
Distribution of $[V_{zn}]$ and $[Al]$ in ZnSe (vertically grown)





Distribution of $[V_{zn}]$ and $[Al]$ in ZnSe (vertically grown)

Vertical destabilized configuration



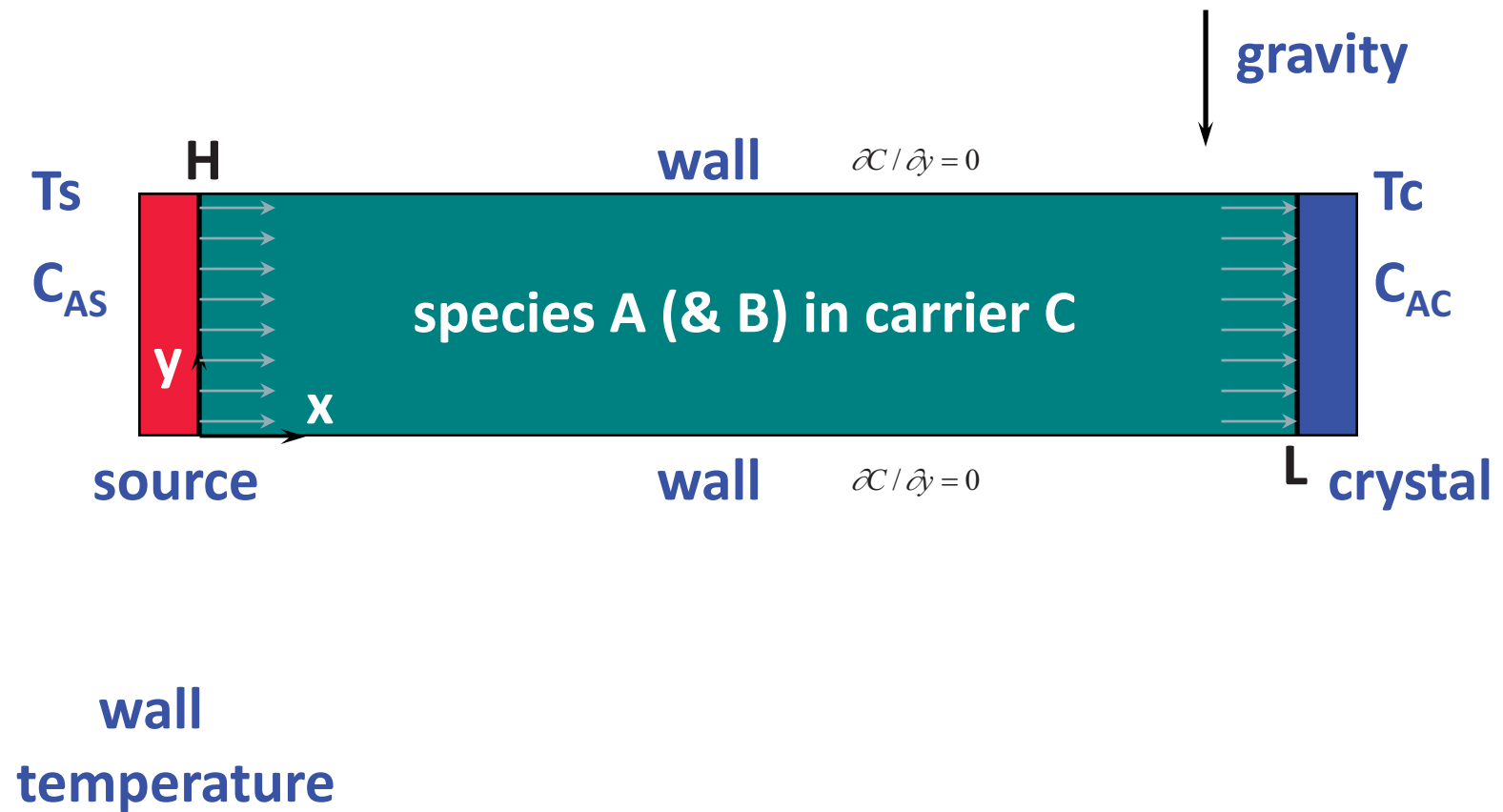


Numerical Modeling of Physical Vapor Transport

- Two dimensional and three dimensional calculations
- Finite element technique - Fidap code
- Thermal and Species induced buoyancy forces
- Compressible or Boussinesq model
- Benchmark -2D ($\text{H}_2\text{-I}_2$ system - PVT growth)
- ZnSe calculations with residual gas
- Benchmark -3D (Natural convection in a cylinder)
- 3-D ZnSe calculations with residual gas
- Ongoing and future work



The Physical Model





Benchmark → the H₂-I₂ System

- benchmark calculations by Rosenberger et al. (J. Crystal Growth 51 426 1981; 67 241 1984; 118 49 1992)
- source temperature $T_s=370.5$ K
- crystal temperature $T_c=358.1$ K
- ampoule pressure : 100 torr
- I₂ (M=254) is the deposited species and H₂ (M=2.016) is inert
- 2-d Cartesian system
- linear wall temperature
- quasi-compressible and Boussinesq calculations
- Peclet number analysis, $Pe \sim 1$ for diffusive flow
- growth rate results



Parameters of ZnSe System with Residual Gas

$$\alpha = 2.9$$

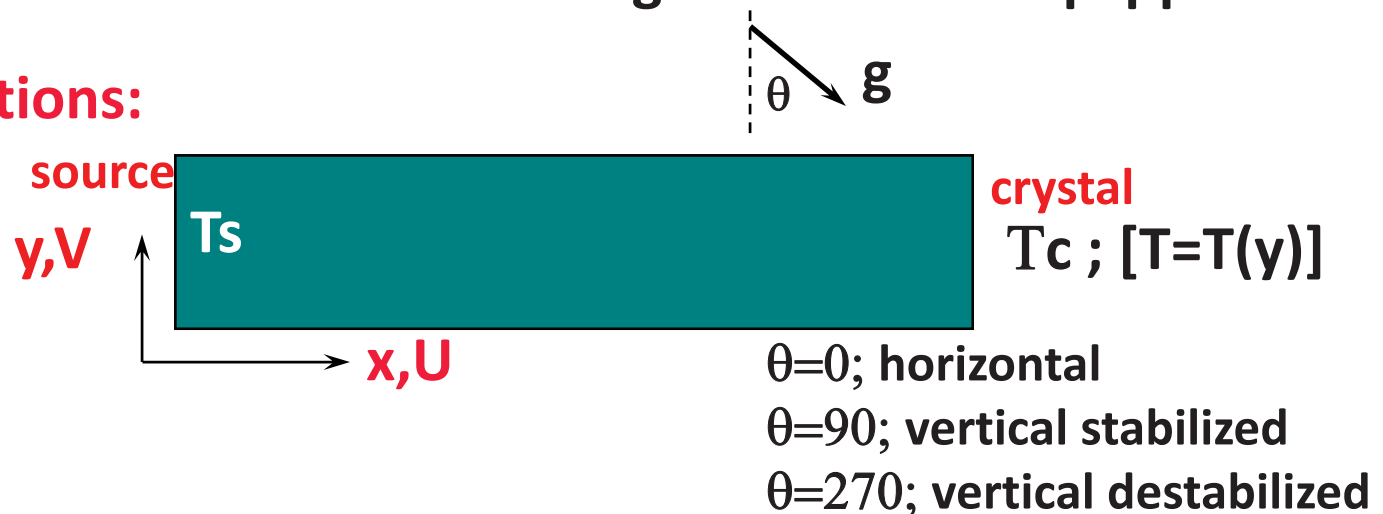
- density, $1.2 \times 10^{-5} \text{ g/cm}^3$
- dynamic viscosity, $4.3 \times 10^{-5} \text{ Pa-s}$
- kinematic viscosity, $36 \text{ cm}^2/\text{s}$
- diffusivity, Zn in N_2 , $64.59 \text{ cm}^2/\text{s}$
- diffusivity, Se_2 in N_2 , $71.46 \text{ cm}^2/\text{s}$
- thermal expansion coefficient, $7.1 \times 10^{-4} \text{ K}^{-1}$
- Prandtl number, 0.439
- Schmidt number, $\text{Sc}_{\text{zn}} = 0.557$
- Schmidt number, $\text{Sc}_{\text{se}} = 0.503$



Velocity Difference Plots - procedure

- calculations for pure diffusion limited conditions, 0g
- calculations for other g conditions, a conditions, etc.
- calculate differences in axial (u) and transverse (v) velocities at all identical grid locations between previous steps; e.g. $U(0g) - U(1g)$ and $V(0g) - V(1g)$
- contour the velocity differences and plot
- determine g-sensitivity
- Note: all calculations were using the Boussinesq approx.

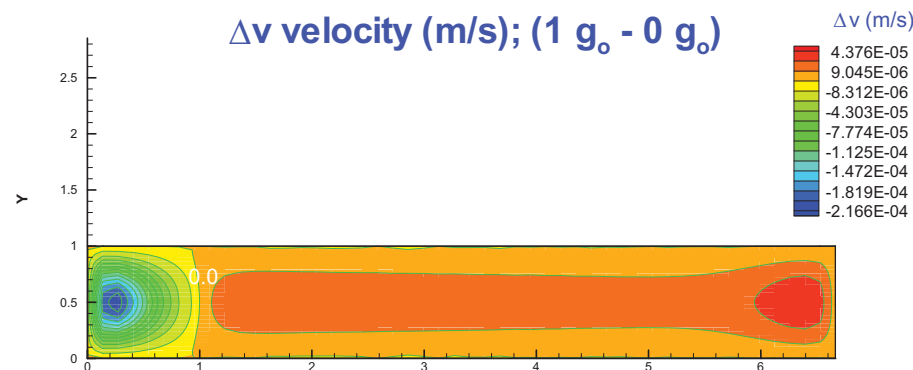
conventions:





Gravity Effect on Velocity Difference (horizontal case)

- g-effects with constant crystal temperature , T_c .
 $\Delta U \sim 0.3 \text{ mm/s}$; $\Delta V \sim 50 \text{ } \mu\text{m/s}$
- g-effects with crystal temperature variation, $T_c = T_c(y)$.
 $\Delta U \sim 0.3 \text{ mm/s}$; $\Delta V \sim 43.75 \text{ } \mu\text{m/s}$



- g-sensitivity (horizontal case) based on max. buoyancy driven flow normal to growth direction is 10% of crystal growth rate (3mm/day or $0.035 \text{ } \mu\text{m/s}$)

transverse acceleration requirement: $\sim 1 \times 10^{-4} g_o$



Gravity Effect on Velocity Difference (vertical case)

- g-effects with crystal temperature variation, $T_c = T_c(y)$.
Stabilized orientation: $\Delta U \sim 23.1 \mu\text{m/s}$; $\Delta V \sim 9.4 \mu\text{m/s}$
- g-effects with crystal temperature variation, $T_c = T_c(y)$.
Destabilized orientation: $\Delta U \sim 18.1 \mu\text{m/s}$; $\Delta V \sim 9.4 \mu\text{m/s}$

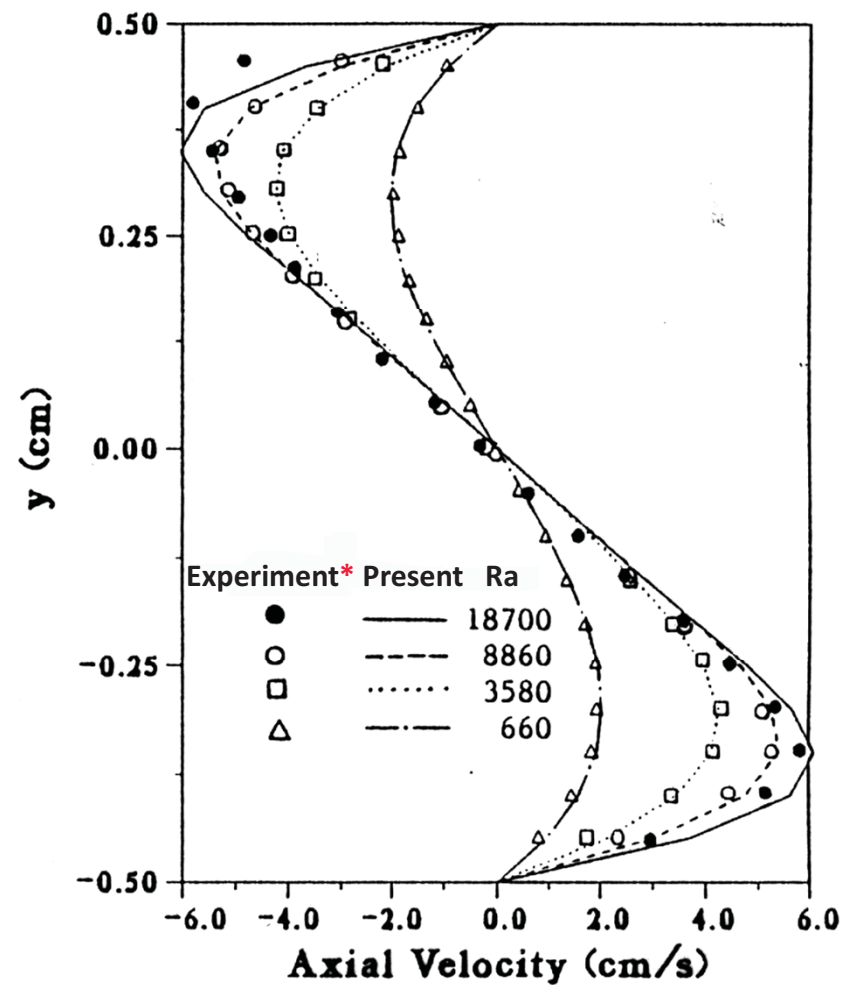
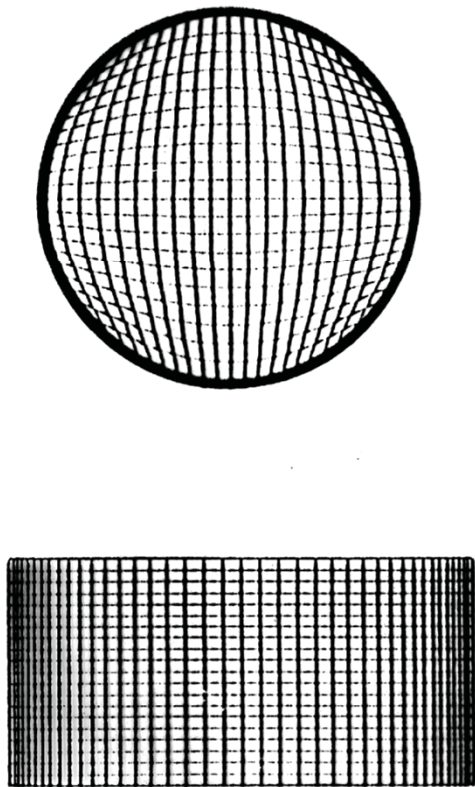
As far as transverse velocity difference is concerned both vertically stabilized and destabilized orientations have similar effects

- g-sensitivity (vertical case) based on max. buoyancy driven flow normal to growth direction is 10% of crystal growth rate (3mm/day or $0.035 \mu\text{m/s}$)

longitudinal acceleration requirement: $\sim 2.7 \times 10^{-3} g_0$



3-D Computational Grid and Code Validation Results



* Schiroky and Rosenberger (1984)



ZnSe with Residual Gas - 3D Calculation Results

- **significant flow observed along the ampoule axis (z-direction) indicative of more deposition in the central area than near the walls**
- **velocity contours in the cross planes(x-y) show appreciable variation only near the end walls (source and crystal)**
- **species (Zn and Se_2) show fairly uniform distributions in the cross planes**
- **predicted crystal growth rate from 2-D and 3-D calculations are in fair agreement**



Summary of Theoretical Calculation

- 2D and 3D calculations performed for ZnSe system
- Residual gas effects considered
- Calculations show that shear flow velocities of **10 to 50 microns/s** are induced by buoyancy effects (290 to 1400 times growth rate)
- g-level requirements established based on time scale analysis **required transverse g level: $< 1.2 \times 10^{-4} g_0$**
required longitudinal g level $< 8.5 \times 10^{-3} g_0$
- It is noted that the Boussinesq model used in the calculations tend to underpredict velocities



Refereed Publications on Vapor Growth

- "Growth Rate of CdS by Vapor Transport in a Closed Ampoule." J. Crystal Growth, 80 333-342 (1987).**
- "Growth and Characterization of CdS Crystals". J. Crystal Growth, 101 221-225 (1990).**
- "Vibronic Spectra of Cu^{+2} in ZnTe". Phys. Rev. B, 46 76-82 (1992).**
- "Growth of ZnTe by Physical Vapor Transport and Traveling Heater Method". J. Crystal Growth, 128 627-632 (1993).**
- "Thermodynamic Analysis and Mass Flux of the HgZnTe-HgI_2 Chemical Vapor Transport System". J. Crystal Growth, 131 574-588 (1993).**
- "Characterization of Growth Defects in ZnTe Single Crystals". Mater. Res. Soc. Symp. Proc., Infrared Detectors - Materials, Processing, and Devices, A. Applebaum and L. R. Dawson (eds.) 299 203-208 (1994).**
- "Photoluminescence of Vapor and Solution Grown ZnTe Single Crystals". J. Crystal Growth, 138 219-224 (1994).**
- "Synchrotron Topography Characterization of ZnTe Single Crystals". Mater. Sci. & Eng. B27, 143 -153 (1994).**
- "Mass Flux of ZnSe by Physical Vapor Transport". J. Crystal Growth, 146 42-48 (1995).**



Refereed Publications on Vapor Growth

- "CdTe I: Solidus Curve and Composition-Temperature-Tellurium Partial Pressure Data for Te-Rich CdTe(s) from Optical Density Measurements". J. Phys. Chem. Solids 57 443-450 (1995).**
- "CdTe II: Defect Chemistry". J. Phys. Chem. Solids 57 451-460 (1995).**
- "Selenium Precipitation in ZnSe Crystal Grown by Physical Vapor Transport". J. Crystal Growth 147 292-296 (1995).**
- "Post-growth Annealing of CdS Crystal Grown by Physical Vapor Transport". J. Crystal Growth 166 721-735 (1996).**
- "Partial Pressures of Zn and Se₂ over ZnSe(s) from Optical Density Measurements". High Temp. and Mater. Sci. 35 215-237 (1996).**
- "Mass Flux and Partial Pressures of ZnSe by Physical Vapor Transport". J. Crystal Growth 166 736-744 (1996).**
- "Analysis of the Zn-Se System". J. Phase Equilibria 17 495-501 (1996).**
- "Mass Flux of ZnSe_{1-x}S_x and ZnSe_{1-x}Te_x by Physical Vapor Transport". J. Crystal Growth 171 516-524 (1997).**
- "Vapor Phase Stoichiometry and Heat Treatment of CdTe Starting Material for Physical Vapor Transport". J. Crystal Growth 183 519-524 (1998).**



Refereed Publications on Vapor Growth

"Segregation Coefficients of Impurities in Selenium by Zone Refining". J. Crystal Growth 187 569-572 (1998).

"Characterization of Semi-insulating CdTe Crystals Grown by Horizontal Seeded Physical Vapor Transport", J. Crystal growth 191 377-386 (1998).

"Heat Treatment of ZnSe Starting Materials for Physical Vapor Transport", To be published on J. Crystal Growth. Ching-Hua Su, W. Palosz, S. Feth and S. L. Lehoczky, "Heat Treatment of ZnSe Starting Materials for Physical Vapor Transport", J. Crystal Growth. 192 386-394 (1998).

"Point Defect Distributions in ZnSe Crystals: Effects of Gravity Vector Orientation during Physical Vapor Transport", J. Crystal Growth 204 41-51 (1999).

"Vapor Growth and Characterization of Cr-doped ZnSe Crystals", J. Crystal Growth 207 35-42 (1999).

"Characterization of ZnSe Single Crystals Grown by Physical Vapor Transport", J. Crystal Growth 208 237-247 (2000).

"Modeling Studies of PVT Growth of ZnSe: Current Status and Future Course", J. Crystal Growth 208 269-281 (2000).

"In-situ Partial Pressure Measurements and Visual Observation during Crystal Growth of ZnSe by Seeded Physical Vapor Transport", J. Crystal Growth 209 687-694 (2000).



Refereed Publications on Vapor Growth

"Contactless Growth of ZnSe Single Crystals by Physical Vapor Transport", J. Crystal Growth 213 267-275 (2000).

"Vapor Growth and Characterization of ZnSeTe Solid Solutions", J. Crystal Growth 216 104-112 (2000).

"Optical Characterization of Bulk ZnSeTe Solid Solutions", J. Appl. Phys. 88 5148-5152 (2000).

"Photoluminescence Studies of ZnSe Starting Materials and Vapor Grown Bulk Crystals", J. Crystal Growth 224 32-40 (2001).

"The Preparation Conditions of Chromium doped ZnSe and Their Effect on the Infrared Luminescence Properties", J. Crystal Growth 225 249-256 (2001).

"Beer Law Constants and Vapor Pressures of HgI_2 over $\text{HgI}_2(\text{s,l})$ ", J. Crystal Growth 235 313-319 (2002).

**"Band Anticrossing in Highly Mismatched Compound Semiconductor Alloys",
Proceeding of the 28th International Symposium on Compound Semiconductors (ISCS2001).**

**"Partial Pressures of Te_2 and Thermodynamic Properties of Ga-Te system",
Thermochimi. Acta. 390 21-29 (2002).**

**"Partial Pressures of In-Se from Optical Absorbance of the Vapor", J. Phase Equilibria 23
43 397-408 (2002).**



Refereed Publications on Vapor Growth

“Composition Dependence of the Hydrostatic Pressure Behavior of the Bandgap of ZnSeTe Alloys”, Phys. Rev. B, 68 033206(1-4) (2003).

“Origin of the Large Bandgap Bowing in Highly Mismatched Semiconductor Alloys”, Phys. Rev. B, 67 035207(1-5) (2003).